

XAFS STUDIES OF THE STRUCTURE OF CARBON SUPPORTED PT ELECTRODES

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There have been a number of studies that have shown that a loss of catalytic activity occurs in the O₂ reduction reaction with time and this is attributed to an agglomeration and increase in the size of the catalyst particles (1). Further studies have demonstrated that the rate of O₂ reduction is dependent on the size of the catalyst particles (2,3). In this work we present data demonstrating that the structure of the Pt catalyst particles supported on carbon are effected by changes in the electrode potential.

In situ x-ray absorption spectroscopy (XAS) measurements were carried out on platinum supported on carbon (Pt/C) electrodes at a series of voltages using a cell described earlier (4). Electrodes were prepared utilizing several sources of Pt/C following a method used previously (5). Two electrolytes 0.1 M HClO₄ and 0.1 M H₂SO₄ were used. A Pd/H reference electrode was used and the data are reported with respect to the RHE. The XAS data were recorded on beam line X-11A at the National Synchrotron Light Source (NSLS). All the data were measured in transmission and a simultaneous measurement was made of a Pt foil (4 μm thick) to insure energy calibration. The zero of energy for the absorption edge of Pt is 11564 eV.

The XAS data were analyzed using the XDAP program. The pre edge was removed and then the background was removed the data was normalized giving us the XAFS spectra. The XAFS spectra were analyzed in the following way. The Pt contribution to each spectrum was determined and then subtracted from the original data resulting in a series of spectra showing the interactions of the Pt with the carbon substrate. The interaction of the Pt with the carbon substrate was then analyzed.

As the voltage was increased from 0.0V to 0.80V the degree of interaction of the Pt with the carbon was found to change. Figure 1 shows the isolated Pt-Pt interaction as a function of the

voltage. The magnitude of the main peak in the figure is proportional to the number of Pt near neighbors and it is clear that the number of near neighbors is decreasing as the voltage goes up. At lower voltages the number of Pt atoms interacting with the carbon is smaller than the number of Pt atoms interacting with the carbon at higher voltages. This suggests that the Pt particles are changing shape as the applied potential is increased. Effects on the electrocatalytic activity may arise from several sources, the change in the particle shape and size and the increased interaction with the carbon substrate shown by the increased number of Pt-C bonds at the catalyst-support interface.

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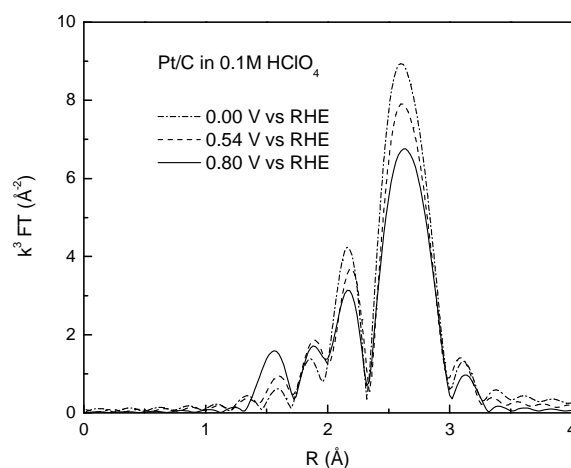


Figure 1

